Compound Formation, Solubility, and Ionization in Fused Salt Mixtures

1. Compound Formation between Aluminium Bromide and Other Bromides.

By

EUGENE D. CRITTENDEN, B.A., M.A.

DISSERTATION

Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University in the City of New York

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The author wishes to express to Professor James Kendall, at whose suggestion this investigation was undertaken, his sincere gratitude for his constant advice and help throughout the course of the work.

The author also desires to thank the other members of the Chemistry Department of Columbia University for their interest and cooperation.

ABSTRACT OF DISSERTATION

1. What was attempted?

2. In how far were the attempts successful?

3. What contributions actually new to the science of chemistry have been made?

1. The attempt was made to demonstrate the application of rules already laid down regarding compound formation and solubility to the case of fused salt mixtures. Solubility data for twenty-five systems in which aluminium bromide was used as a solvent for other bromides have been presented.

2. It has been shown that compound formation and solubility for salt mixtures varies in accordance with the "diversity" of the positive radicals, reaching a *minimum* in the vicinity of aluminium and increasing markedly in either direction from this.

3. (a) The influence of subsidiary factors, such as unsaturation, valence, and temperature of fusion on the formation of addition compounds has been outlined.

(b) The effect of internal pressure and atomic volume on miscibility and compound formation has been fully discussed.

(c) In the course of the investigation thirty-two new compounds have been isolated.

COMPOUND FORMATION, SOLUBILITY, AND IONIZATION IN FUSED SALT MIXTURES

1. Compound Formation between Aluminium Bromide and Other Bromides.

In a recent series of papers by Kendall and his coworkers[1] extensive evidence has been presented correlating compound formation, solubility, and ionization in solution. It has been postulated that compound formation is most marked and consequently solubility is most extensive in systems where the radicals are most diverse in character; the criterion of diversity being their position in the electrode potential series. Thus Landon[2] and Davidson[3] found in the systems sulfuric acid-metal sulfate that potassium and silver, the metals farthest removed from hydrogen in either direction, gave the greatest compound formation. This "diversity" rule has been tested for a large number of systems and has been found to hold without marked exception. A few minor discrepancies, however, have come to light; and in order to explain these, several additional factors, such as atomic volume, internal pressure, and unsaturation, which will be taken up more fully below, have been mentioned.

In order to obtain additional evidence regarding the rules already laid down, it was thought best to study next systems where double salts should be formed. For this purpose, as reference, a salt of low melting point was desirable as well as one whose metallic constituent was above hydrogen in the "electrode potential" series and whose radicals were as diverse as possible. Aluminium bromide seemed to give promise of fulfilling such requirements, and twenty-five systems using this salt as a solvent have been investigated by the freezing point method, using sealed bulbs throughout. It was again deemed advisable to follow the order of elements as given by the "electrode potential" series, although this is known to be in error in several instances.[4]

The "diversity" factor has been found to hold as well for these systems as for those previously reported. This "diversity" factor, although the main point upon which to base any comparison of results in systems where compound formation occurs, must be joined up with several subsidiary factors such as internal pressure, atomic volume, unsaturation of the radicals, and the temperature of fusion of the pure substances in order to obtain a satisfactory correla-

[1] See Kendall and Davidson (A.W.), J.A.C.S., *43* 980 (1921) for references to earlier work.

[2] Landon, Columbia University Dissertation, 1920.

[3] Davidson, Columbia University Dissertation, 1920.

[4] Kendall, Davidson, and Adler, J.A.C.S., *43* 1501 (1921).

tion of this work with the results previously given. It is with this object in view that the present work is presented.

Previous Work on Fused Salts

The literature is crowded with examples of double salts, but far too often the work was carelessly done or carried out in the presence of solvents, no account of whose action was taken. No systematic investigation on binary systems of fused salts has ever been performed with the idea of correlating fact with theory. Many isolated systems in aqueous solution are recorded, but most often the compounds reported were hydrates of uncertain composition and stability or else haphazard mixtures were made up and each result called a compound.[1] Obviously, such results can not be used in a rigorous study of solubility rules. That double salts are extensively formed in solutions is evidenced by the large number of different types of such salts reported. Such cases as the double cyanides with potassium cynide, the alums, and the platinocyanides furnish only a few examples of such types. It is interesting to note that in the above-mentioned cases the greatest number and the most stable compounds are formed with those salts whose metallic constituents are most diverse from the reference metal, hence presenting further evidence that the diversity factor is the main one in any consideration of systems where compound formation occurs. Thus we find potassium argentocyanide, potassium and barium platinocyanides, and the alums, with the alkali metals, are the most stable compounds in their respective systems.

Numerous double bromides are also recorded, but here again the method of their isolation and study makes their composition so uncertain that they are not included in a discussion here. Miller[2] has correlated the data for chloride systems and it is apparent that the bromides do not present a far different case. It was hoped that the present work would lead towards the establishment of the position of fused salts in the general scheme of compound formation, solubility, and ionization already presented.[3] Such hopes have been realized for the cases of compound formation and solubility when account is taken of the subsidiary factors; i.e., atomic volume, internal pressure, valence, etc., which, together with the "diversity" factor already fully discussed,[4] constitute the basis for such comparisons.

Choice of Aluminium Bromide as a Solvent

Most salts present so many shortcomings as solvents that the choice of one suitable to fulfil a given set of conditions is by no

[1] An interesting case is found in the work of Baud, Ann. Chim. Phys., (8) *1* 8, (1904).

[2] Miller, Columbia University Dissertation (1922).

[3] Kendall and Gross, J.A.C.S., *43* 1416 (1921). Also Kendall and Davidson, J.A.C.S., *43* 980 (1921).

[4] Kendall, Booge, and Andrews, J.A.C.S., *39* 2303 (1917).

means easy. In order to make the present investigation as thorough as possible, the careful selection of a salt with just the proper set of characteristics was necessary. This salt must have a low internal pressure, be non-polar in character, have a low melting point, and possess radicals which are as widely diverse as practicable. A salt of a higher valence type than uni-univalent was also desirable, as well as one whose metallic constituent had a position well above hydrogen in the "electrode potential" series.

After an extended search, aluminium bromide was finally selected as most nearly fulfilling the above requirements. It has a low melting point, a low internal pressure as evidenced by its position in a table of relative internal pressures,[1] is slightly polar, and satisfies the requirements of diversity and position of its radicals. Kablukow[2] and Menschutkin[3] have already shown that aluminium bromide is an excellent solvent for a large number of organic substances. They have isolated several compounds, but only in those systems where such a result would be expected from the rules already laid down. Isbekow and Plotnikow[4] in a paper entitled "Aluminium Bromide as a Solvent" have presented considerable evidence of a qualitative nature in regard to the solvent action of aluminium bromide for inorganic salts. These writers did not make a complete study of any of the systems presented, but were only interested in relative solubilities with the idea of using such information later as a basis for conductivity determinations. Conductivity results have been given for three systems, but the discussion of their bearing on this work will be left till after a discussion of the present results.

Experimental Procedure

In the present investigation solutions of the bromides of Li, Na, K, NH_4, Ag, Ca, Ba, Mg, Zn, Cd, Hg′, Hg″, Tl′, C, Sn″ ″, Sn″, Pb″, As″ ′, Sb″ ′, Bi, P″ ′, Cr″ ′, Mn″, Fe″, and Ni in aluminium bromide have been studied by the freezing point method.[5] The solubilities in all but a few cases; i.e., Ni and Cr″ ′, were quite considerable and the curves have all been determined at least to 20%, with the exception of the two above. With the alkali metals, for example, the curves have been extended beyond 50%, after which the slope of the curve becomes very steep; a point which will be discussed under the lithium system. In other cases the curves were carried at least far enough to give evidence of a compound such as $2AlBr_3$, MBr_x, if such existed. With bromides of low melting point the complete curves were determined.

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[1] See page 48 for table of internal pressures of bromides.
[2] Kablukow and Khanow, Chem. Zentral Blatt, (1) 419-32, (1910).
[3] Menschutkin, J. Chim. Phys., *10* 552 (1911).
[4] Isbekow and Plotnikow, Zeit, Anorg. Chem., *71* 328 (1911).
[5] Kendall and Booge, J.A.C.S., *38* 1718 (1916). Also Kendall and Landon, J.A.C.S., *42* 2131 (1920).

Due to the exceedingly hygroscopic nature of aluminium bromide, sealed bulbs were used throughout and the preparation of such tubes confined to clear, cold, dry days. For this purpose it was thought advisable to depart from the method of sealing on a handle after preparing and filling the bulb, as had been done by previous workers.[1] The method adopted was to blow a bulb on the end of a Pyrex tube from 12-15 cms. in length, depending on the temperature at which the tube was to be used.[2] The diameter of the tube also varied from 3-6 mms., depending on the type of substance—liquid or solid—to be used. The tubes were all carefully cleaned and dried before filling. The tubes were first weighed empty and then the substance to be determined was added. After reweighing, the aluminium bromide, which was kept in a weighing bottle over phosphorous pentoxide, was quickly added and the tube sealed in a blast lamp. After cooling, the tubes were washed, dried, and reweighed. From the weights so obtained, the percentage composition could be readily computed. After short experience little trouble was found in judging the proper quantities of the two components needed to make up a desired composition. Great care was exercised to insure no adherence of the substance to the upper part of the tube, since this would introduce a serious error. With a very fine powder, such as mercurous bromide, it was found necessary to use a clean funnel brush to remove adhering powder from the upper part of the tube. Usually, however, light tapping was found sufficient, since most substances were used as crystals not too finely powdered.

The tube, after the final weighing, was immersed in a bath whose temperature was carried several degrees beyond the disappearance of the last trace of solid. Thorough agitation was maintained by tilting and shaking. Each point was determined at least twice, the disappearance of the last trace of crystals being taken as the melting point for that composition.

The bath in which the bulb was placed for the determination of the melting point varied with the temperature range in which the point lay. The baths used with their respective temperature ranges were:

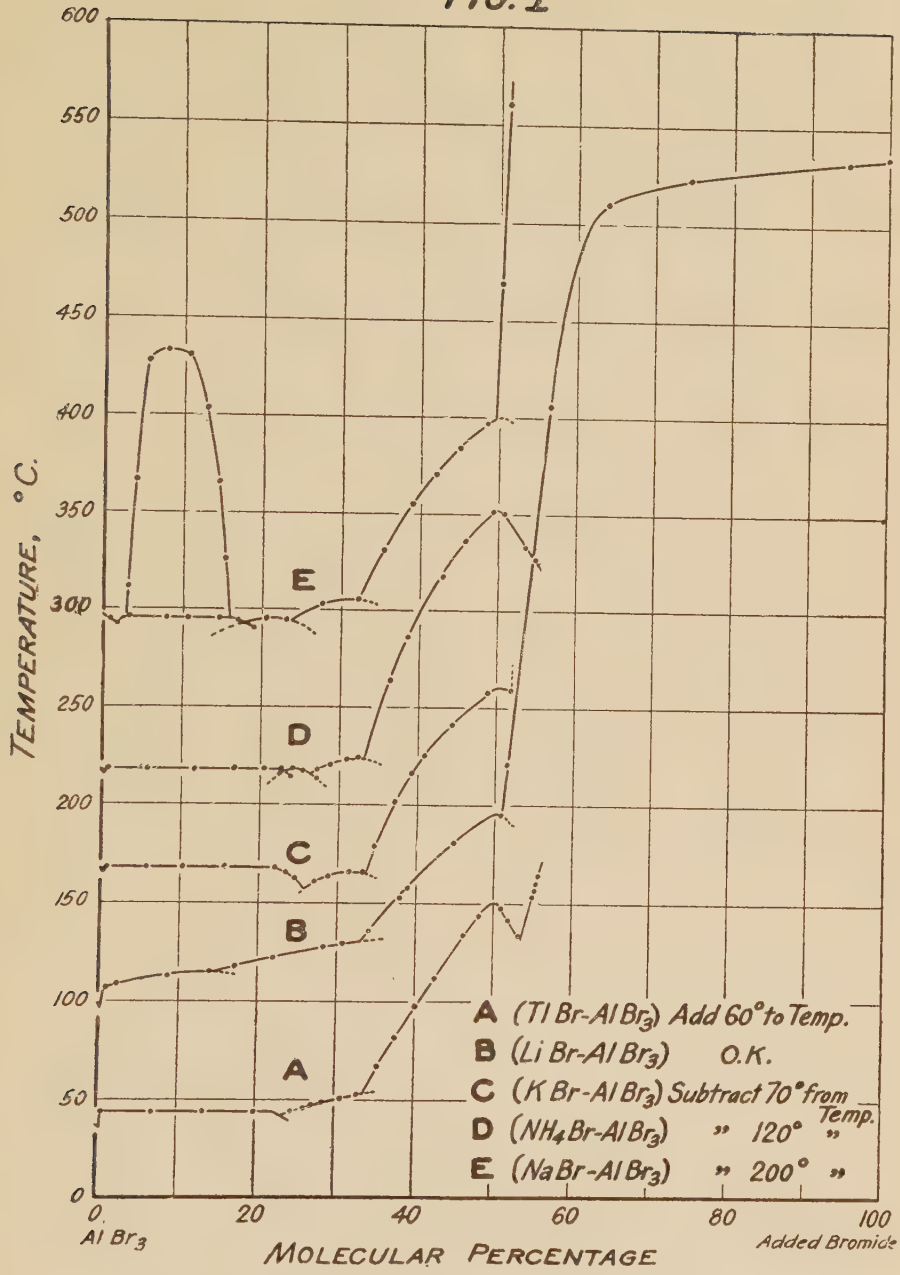
HNO_3 and Ice	—25°— 0°
Water	0°— 30°
Sulfuric Acid	30°—110°
30% $(NH_4)_2SO_4$ and 70% H_2SO_4	110°—200°
$NaNO_3$, KNO_3, and $Ca(NO_3)_2$	200°—310°
[3]$NaNO_3$ and KNO_3	310°—550°

[1] Davidson, Columbia University Dissertation, (1920).

[2] Longer tubes were found necessary for temperatures above 180°.

[3] See Menzies and Nutt, J.A.C.S., *33* 1366 (1911), for eutectic mixtures of nitrates.

FIG. I


TEMPERATURE, °C.
600
550
500
450
400
350
300
250
200
150
100
50
0
E
D
C
B
A
0
Al Br3
20
40
60
80
100
Added Bromide
MOLECULAR PERCENTAGE
A (Tl Br-Al Br3) Add 60° to Temp.
B (Li Br-Al Br3) O.K.
C (K Br-Al Br3) Subtract 70° from Temp.
D (NH4 Br-Al Br3) " 120° "
E (Na Br-Al Br3) " 200° "

In work of such wide range considerable attention had to be paid to the factors affecting thermal equilibrium between the tube, thermometer, and the bath. It was found necessary to observe the following precautions in order to avoid errors which would appreciably affect the freezing points.

1. The tube and bath were stirred constantly during the determination of a point.
2. The temperature was changed slowly enough to maintain[1] as nearly as practicable thermal equilibrium during the heating process.
3. The bulbs were sufficiently thin to prevent lag when the above precautions were observed.[2]
4. The air space in the bulbs was as small as possible to avoid excess pressure.

At higher temperatures draughts and radiation were excluded by the use of an asbestos shield surrounding the bath. Windows were provided in this to permit observation.

Measurement of Temperature

Temperatures were measured by means of two mercury thermometers graduated in fifths of degrees, having ranges 0°—200° and 200°—300° respectively. For temperatures above 300° a base metal pyrometer, with a low resistance, direct reading galvanometer was used which had a scale graduated in 10° intervals. The accuracy and corrections for the thermometers and pyrometer were determined by the use of a platinum resistance thermometer[3] carefully calibrated against the freezing and boiling points of water and the boiling point of sulfur by the method prescribed by the Bureau of Standards.[4] The value of "delta" as found was 1.63, which is sufficiently low to permit the use of the thermometer as a standard.[5] The standard temperature-resistance curve was plotted by means of the data obtained and the temperature for any resistance could then be read directly from this. Intermediate points were determined by means of the formula: $\frac{R}{R_0} = 1 + at + bt$,[2] where R_0 is the resistance at 0°, R is the resistance at the temperature t,

[1] About 0.2° per minute was the average rate of heating. This was subject to slight variation depending on the slope of the curve. Thus for a steep slope the rate of heating was slightly increased, while for the reverse case it was diminished.

[2] This is shown by the smoothness of the curve for any given phase.

[3] For the use of the thermometer and accessories, the author wishes to express his thanks to Prof C. D. Carpenter.

[4] For the method of assembling and use, see Reprint No. 124, Bureau of Standards. Also J.A.C.S., *41* 748. (1919).

[5] The standard value for pure platinum is 1.50, but a slightly higher value does not alter the constants *a* and *b* sufficiently to affect this work or any other except the most precise.

and a and b are constants determined from the standard data for the thermometer.

The thermometers were immersed to the same depth during the calibration as during their use throughout this investigation. By determining the resistance at 10° intervals, the necessary correction for any temperature could be easily found by taking the difference between this resistance and that obtained from the standard calibration curve. Thus both stem correction and standardization for the thermometers were directly determined at the same time. By plotting these corrections against the temperatures, the necessary correction for any point on the thermometers could be read directly. In the case of the pyrometer, the calibration was made for 50° intervals since relative values only were required above 300°.

PRECISION OF MEASUREMENTS

The freezing points of mixtures prepared by the method described above and determined by means of one of the thermometers or the pyrometer have definite precision values. These values depend on the temperature range in which the point lies and also on the slope of the curve. The approximate limits of accuracy obtained in this work are as follows:

Sealed bulb.....	0°—100°	0.3°—0.5°
Sealed bulb.....	100°—200°	0.5°—1°.0
Sealed bulb.....	200°—300°	1°.0—2°.0
Sealed bulb.....above	300°	2°.0—5°.0

The higher limits above refer to the *accuracy* of the temperature measurements, taking into account all probable sources of error; i.e., constant and personal errors, as well as errors of method. The lower limit expresses the *reproducibility* of the values.

The composition data have an accuracy of one-tenth of a molecular per cent, the hygroscopic nature of most of the salts employed making it impossible to obtain better values.

EXPERIMENTAL RESULTS

Preparation of Aluminium Bromide.

Pure aluminium bromide was prepared by dropping 30 mesh aluminium slowly into bromine to avoid too vigorous action When the action was complete, excess aluminium was added and the product digested for an hour over a low flame. The salt was distilled twice from excess aluminium and then transferred by distillation into a large flask with side arm and ground glass stopper. Throughout this work a calcium chloride tube was connected to the side arm of the flask.

In this flask the aluminium bromide was sublimed on a water bath containing salt solution which boiled above 105°. When sufficient product had collected, it was shaken loose and transferred to a

clean, dry weighing bottle, which was kept over phosphoric anhydride in a vacuum desiccator until used. Only small quantities were prepared at one time due to the rapid decomposition of the salt on exposure to the air. The salt becomes light yellow after it has taken up even a trace of water, and this was used as one criterion of purity, no sample being used after the first trace of yellow appeared.

The salt was obtained in white shining plates which melted uniformly at 97°.1. This value is considerably higher than those previously recorded.[1] Although not ultra pure,[2] the salt was sufficiently pure for freezing point work. Throughout this investigation the melting point of the aluminium bromide never fell below 96°.8, as was shown by tests made at frequent intervals. By use of the thermal method, a new form of aluminium bromide with a transition point at 70°.2 was found. This new modification has been confirmed in several systems below.

SYSTEM LiBr—$AlBr_3$

Pure lithium bromide was prepared from a U.S.P. sample by precipitating the carbonate and redissolving this in just sufficient c.p. HBr to affect solution. The solution was evaporated to small volume and allowed to crystallize. The mother liquor was removed as completely as possible by decantation and the crystals of the hydrate transferred to a Pyrex tube—1 cm. by 10 cm. The tube was heated slowly at first to decompose the hydrates and then rapidly to a temperature above 600°. After cooling, the tube was carefully broken and only the large lumps taken in order to avoid contamination by glass. The salt was kept in a glass stoppered bottle in an oven at 120° during the whole course of the work on this system.[3] Due to the exceedingly hygroscopic nature of lithium bromide, tubes for this system were prepared only on 'exceptionally' clear, dry days.

No previous work on this system could be found in the literature. The data for this system are given below and in Fig. 1, B.

(a) Solid phase—$AlBr_3$.

%LiBr.	0.00
[4]T.	97.1

(b) Solid phase—$7AlBr_3$,LiBr.

%LiBr.	.62	2.0	4.3	8.7	11.1	14.0	16.2
T.	107.2	108.2	109.8	112.4	113.6	114.6	113.0

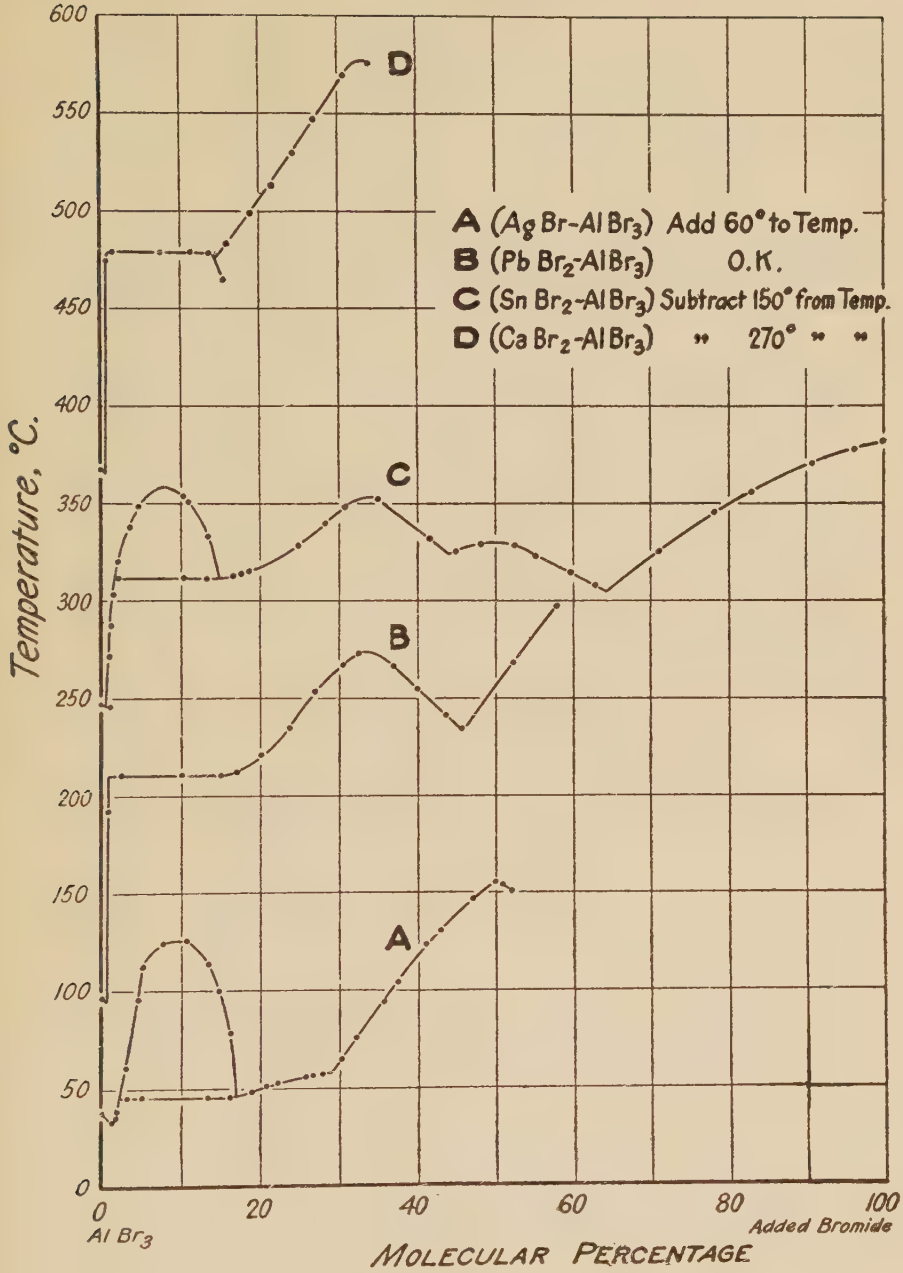
[1] Varying values are given by different investigators. Thus 90°, Weber, Pogg. Ann. *103*, 204. (1857); 93°.0, Abegg, Handbuch Anorg. Chem., *3* (1) 75; 96°.0, Menschutkin, loc. cit.

[2] Richards and Krepelka, J.A.C.S., *43* 2221 (1920) have used this salt for atomic weight determinations, but they report no value for the melting point.

[3] This general policy was adopted for all systems where the salts were very hygroscopic and possessed a sufficiently high fusion point, (e.g. above 150°).

[4] T. is the temperature of the disappearance of the last trace of crystals; taken as the fusion point for that composition.

FIG. II


600
550
500
450
400
350
300
250
200
150
100
50
0
Temperature, °C.
A (Ag Br-Al Br3) Add 60° to Temp.
B (Pb Br2-Al Br3) O.K.
C (Sn Br2-Al Br3) Subtract 150° from Temp.
D (Ca Br2-Al Br3) " 270° " "
A
B
C
D
0
20
40
60
80
100
Al Br3
Added Bromide
MOLECULAR PERCENTAGE

(c) Solid phase—$2AlBr_3$,LiBr.								
%LiBr.	14.0	17.1	22.0	25.7	27.8	28.7	30.6	
T.	114.6	117.7	121.9	125.2	126.7	127.9	129.4	
(d) Solid phase—$AlBr_3$,LiBr.								
%LiBr.	34.2	37.9	39.1	40.7	44.9	46.8	48.4	50.6
T.	135.5	152.2	157.9	164.5	180.7	186.7	192.5	195.4
(e) Solid phase—LiBr.								
%LiBr.	51.4	56.7	63.9	74.6	90.0	100.0		
T.	221.4	405.0	510.0	523.0	532.0	535.0		

The composition in this and following systems is expressed throughout in molecular percentages. It was deemed advisable to carry the work far enough to complete the curve since it is rising sharply beyond the 50% compound. As had been expected, no compound with more than 50% LiBr was found in this system, a point to be discussed later. The curve rises rapidly till 70% LiBr is reached, after which the rate of change is slow up to the melting point of pure lithium bromide at 535°.

Three new compounds, 7 $AlBr_3$, LiBr; $2AlBr_3$, LiBr; and $AlBr_3$, LiBr, have been isolated in this system. The first is stable just up to its maximum at 114°.4, the second undergoes transition to the equi-molecular compound before its maximum is reached, while the third is a stable compound with a M.P. 197°.

It will be noted from the figure (Fig. 1, B) that the curve rises sharply at first with small changes of composition, but soon flattens out. This behavior is typical for cases where two liquid layers are present in the metastable region.[1]

SYSTEM NaBr-$AlBr_3$

The salt used was a c.p. sample recrystallized once from distilled water and carefully dried in an oven at 120°.

Isbekow and Plotnikow[2] have found that NaBr is quite soluble in aluminium bromide even at 100°. They report the breaking up of mixtures with small percentages into two liquid layers with a critical temperature of mixing near 230°. They, however, report no compounds.

The present work confirms the existence of a two liquid layer region with low percentages of NaBr. The solid phase separating out from this region has been shown to contain an unstable compound[3] as evidenced by the double eutectic.

The data for this system are given below and in Fig. 1, E.

(a) Solid phase—$AlBr_3$.					
%NaBr.	0.0	0.7	0.9	1.4	1.7
T.	97.1	95.2	94.8	93.6	93.0

[1] See Miller, loc. cit., for an interesting case of this kind.

[2] Isbekow and Plotnikow, loc. cit.

[3] For a discussion of unstable compounds of this very rare type, see Roozeboom, Heterogene Gleichgewicht, *2* (2) 168.

(b) Solid phase—$xAlBr_3,yNaBr$.

%NaBr.	1.9	2.2
T.	93.9	94.6

(c) Two liquid layers; solid phase disappearing at 95°.4.

%NaBr.	3.1	4.0	5.4	7.8	10.45	12.8	14.5	15.3
[1] T. of Coales	110.9	166.4	227.1	231.9	230.5	202.7	166.9	125.6

(d) Solid phase—$xAlBr_3,yNaBr$[2].

%NaBr.	17.0	17.7	18.4	19.0
T.	94.2	93.0	91.6	90.4

(e) Solid phase—$7AlBr_3,2NaBr$.

%NaBr.	16.9	18.4	20.5	21.5	22.1	23.4
T.	92.8	94.0	95.4	95.8	96.0	95.1

(f) Solid phase—$2AlBr_3,NaBr$.

%NaBr.	24.03	25.1	27.5	31.9
T.	94.8	98.2	102.4	104.5

(g) Solid phase—$AlBr_3,NaBr$.

%NaBr.	32.6	35.3	36.8	38.9	42.0	45.0	48.6	50.3
T.	108.8	131.2	141.5	154.8	170.4	184.0	196.4	200.5

(h) Solid phase—NaBr.

%NaBr.	50.3	51.1
T.	269.0	360.0

As will be seen from the diagram (Fig. 1, E), the curve is rising rapidly beyond the 50% composition as was the case with the lithium system above. This precludes the possibility of a higher compound than an equimolecular since the solid phase separating is unquestionably NaBr.[3]

Four new compounds not previously reported have been found in this system. The unstable compound of uncertain composition in the two layer region has already been mentioned. The compound $7AlBr_3$, 2NaBr is stable at its maximum and has a melting point of 95°.6, while the compound $2AlBr_3$, NaBr undergoes transition to the equimolecular before its maximum is reached. The latter is just stable at its maximum and has a melting point of 201°.

SYSTEM KBr-$AlBr_3$

The salt used was a c.p. sample recrystallized once from distilled water and carefully dried.

Isbekow and Plotnikow[4] have found that this salt is also quite soluble in aluminium bromide at 100°, giving two liquid layers in the low percentages. They were unable to determine the critical temperature of mixing on account of its high value (above 360°). They report no compounds in their work. Weber[5] found an equi-

[1] Temperature of coalescence is that temperature at which one of the two liquid layers disappears.

[2] Throughout this work the above type of formula will be used to designate the compound of uncertain composition in the two layer region.

[3] The behavior of this system beyond the 50% composition is similar to that of lithium in the same region where it has been shown that no compounds exist.

[4] Isbekow and Plotnikow, loc. cit.

[5] Weber, Pogg. Ann. *103* 259.

molecular compound by fusing together potassium and aluminium bromides, distilling off the excess aluminium salt and analyzing the residue.

This investigation confirms the work of both Isbekow and Weber as well as adding two new compounds, an unstable one in the two layer region and $2AlBr_3$, KBr, both not previously reported.

The data for this system are given below and in Fig. 1, C.

(a) Solid phase—$AlBr_3$.

%KBr.	0.00							
T.	97.1							

(b) Solid phase—$xAlBr_3$,yKBr.

%KBr.	0.33							
T.	97.5							

(c) Two liquid layers; solid phase disappearing at 98°.1

%KBr.	0.86	19.4						
T. of C.	265.9	189.6						

(d) Solid phase—$xAlBr_3$,yKBr.

%KBr.	23.3	24.7						
T.	95.6	92.2						

(e) Solid phase—$2AlBr_3$,KBr.

%KBr.	25.8	27.1	28.8	31.6	33.2			
T.	88.6	90.8	93.0	95.5	95.8			

(f) Solid phase—$AlBr_3$,KBr.

%KBr.	34.7	37.3	39.5	41.0	44.5	47.4	49.0	51.26
T.	109.0	130.6	145.9	154.6	171.4	181.7	188.4	189.6

(g) Solid phase—KBr.

%KBr.	52.0	54.7	
T.	188.8	above 390.	

Here again the curve rises rapidly beyond the 50% composition, KBr separating as the solid phase. With the exception of the equimolecular compound, which gets slightly beyond the 50% composition, the compounds are not stable at their maxima. The compound $2AlBr_3$, KBr undergoes transition to the equimolecular compound at 96° and 33%. The equimolecular compound melts at 191°.5.

SYSTEM NH_4Br-$AlBr_3$

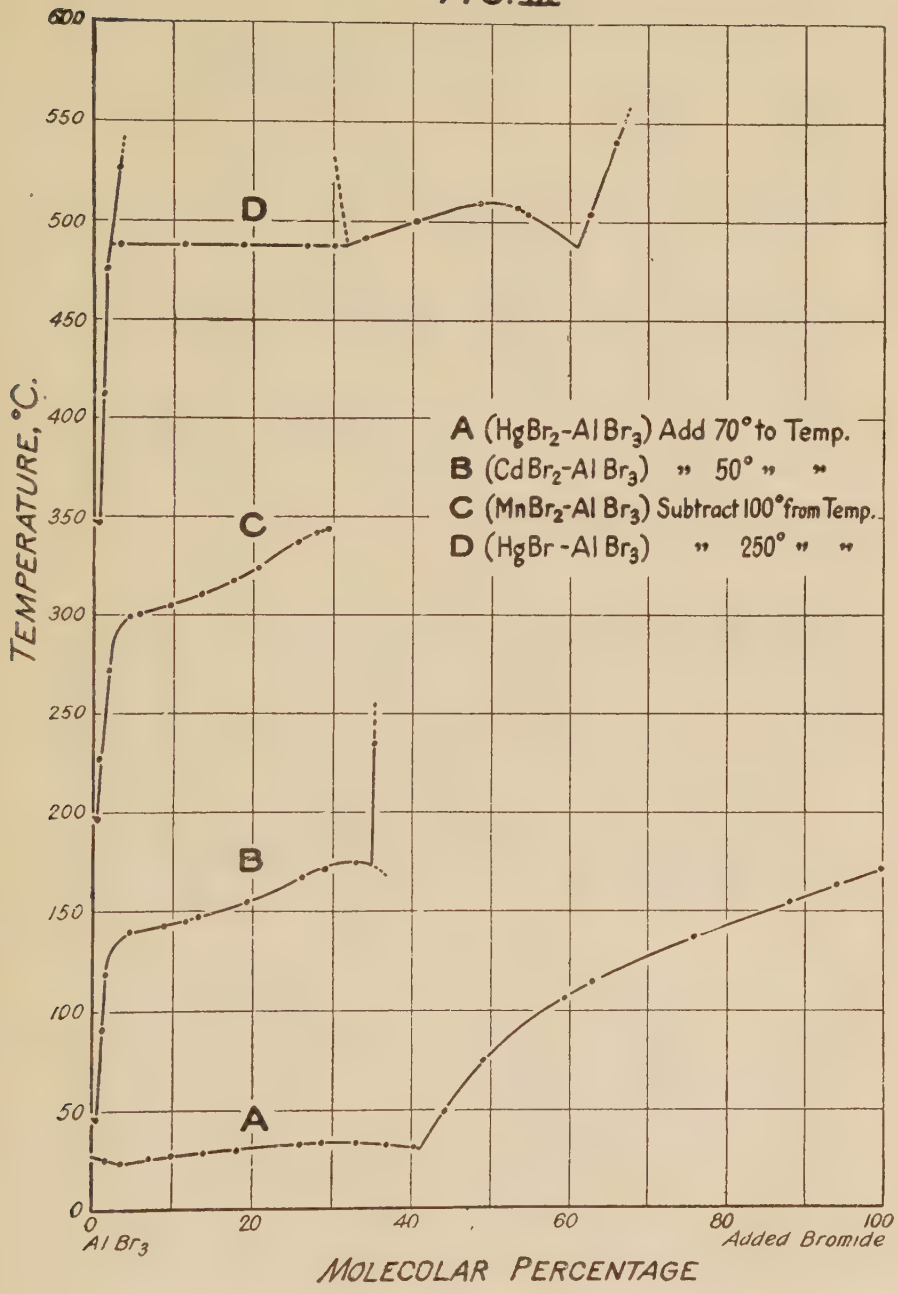
This salt was prepared from a c.p. sample by one recrystallization from distilled water and subsequent thorough drying.

Isbekow and Plotnikow[1] found exactly the same behavior for this salt in aluminium bromide as for potassium; a result to be expected from their similar action previously noted.[2] It was impossible to cause the coalescence of a mixture containing only 5% NH_4Br even at the boiling point of aluminium bromide (365°). The critical temperature of mixing for this system must lie considerably higher than this, thus confirming the observation of Isbekow. Four new compounds not previously recorded have been isolated. As with

[1] Isbekow and Plotnikow, loc. cit.

[2] See Kendall and Landon, loc. cit., for a comparison of the corresponding sulfate systems. Also Kendall and Adler, loc. cit., for the formate systems.

FIG. III


600
550
500
450
400
350
300
250
200
150
100
50
0
TEMPERATURE, °C.
D
C
B
A
A (HgBr2-AlBr3) Add 70° to Temp.
B (CdBr2-AlBr3) " 50° " "
C (MnBr2-AlBr3) Subtract 100° from Temp.
D (HgBr-AlBr3) " 250° " "
0
20
40
60
80
100
AlBr3
Added Bromide
MOLECOLAR PERCENTAGE

potassium, an unstable compound exists in the two layer region, showing this to be the rule for the alkali metals investigated.[1]

The data for this system are given below and in Fig. 1, D.

(a) Solid phase—$AlBr_3$.

%NH_4Br.	0.00						
T.	97.1						

(b) Two liquid layers; solid phase disappears at 98°.0.

%NH_4Br.	0.52	0.8	20.45				
T. of Coales.	160.5	236.5	159.5				

(c) Solid phase—$xAlBr_3$,yNH_4Br.

%NH_4Br.	24.0						
T.	94.8						

(d) Solid phase—$3AlBr_3$,NH_4Br.

%NH_4Br	22.8	23.1	23.8	25.2	27.3		
T.	96.6	96.9	97.5	97.3	92.7		

(e) Solid phase—$2AlBr_3$,NH_4Br.

%NH_4Br.	27.3	28.2	31.0	32.4	32.9	33.5	
T.	98.1	99.9	103.2	103.8	104.0	103.6	

(f) Solid phase—$AlBr_3$,NH_4Br.

%NH_4Br.	36.3	38.5	43.0	46.1	49.5	50.7	53.4
T.	143.8	166.1	197.2	214.0	230.5	229.8	213.6
	54.7						
	207.5						

(g) Solid phase—NH_4Br.

%NH_4Br.	57.1
T	above 360°.

As has been found with the other alkali metals, the curve rises steeply beyond the equimolecular compound, depositing in this case pure NH_4Br. It was impossible to obtain a tube with sufficiently little NH_4Br so that two layers were not present. To find the limit of the two layer region in this part of the curve, it would be necessary to employ the Beckman freezing point method, work which is beyond the scope of this investigation.

In this system two of the compounds—the $3AlBr_3$, NH_4Br and the equimolecular—are stable at their maxima and have melting points 97°.8 and 232°, respectively. The compound $2AlBr_3$, NH_4Br gets just beyond its maximum before transition to the equimolecular compound occurs. The melting point for this compound is 104°.2.

SYSTEM AgBr-$AlBr_3$

Silver bromide was prepared by precipitating a solution of c.p. HBr with silver nitrate in a dark room. The precipitate was washed thoroughly by decantation and transferred to a filter paper, where it was rewashed till free from bromide ion. The product was carefully dried at 120° and then heated to 200° to decompose any compounds between AgBr and HBr which might be present. The salt was preserved in a bottle well protected from the light and tubes for this system were made up only on days when it was dry but not too light.

[1] The anomalous behavior of lithium will be taken up under the discussion of results.

In this system Isbekow and Plotnikow[1] report a two liquid layer region similar to the ones with the alkali metals. These writers give 180° as the critical temperature of mixing, but mention no compounds. No other work on this system could be found.

The data are given below and in Fig. 2, A.

(a) Solid phase—$AlBr_3$.

%AgBr.	0.00	1.1	1.3
T.	97.1	94.2	93.4

(b) Solid phase—(?), probably $2AlBr_3,AgBr$.

%AgBr.	1.5	1.6
T.	95.3	98.2

(c) Two liquid layers, solid phase disappears at 105°.9.

%AgBr.	3.0	4.5	5.0	7.6	13.4	14.7	16.2
T. of Coales.	120.4	156.3	161.9	183.6	173.0	159.7	139.7

(d) Solid phase—$2AlBr_3,AgBr$.

%AgBr.	18.7	20.7	22.1	25.6	26.4	27.8
T.	108.6	111.3	112.8	115.6	116.9	117.8

(e) Solid phase—$AlBr_3,AgBr$.

%AgBr.	30.2	32.0	35.6	37.3	39.2	40.9	42.7	46.8
T.	125.2	135.0	154.6	164.1	174.1	182.3	189.5	206.8
%AgBr.	50.2	50.6	52.0					
T.	215.8	214.2	210.3					

(f) Solid phase—AgBr.

%AgBr.	54.9
T.	319.0

The curve is rising rapidly beyond the 50% composition with the separation of the neutral salt, as was the case with the alkali metals. There is no evidence in this system of an unstable compound in the two layer region as evidenced by the non-existence of a second eutectic[2] at the higher composition end of the two layer region.

The results here recorded show the existence of two new compounds—$2AlBr_3$, AgBr and $AlBr_3AgBr$. The first is unstable at its maximum, undergoing transition at 118°.4 to the equimolecular compound. The second compound has a melting point of 215°.6 and is stable well beyond its maximum. The critical temperature of mixing was found to be 186°, agreeing well with the value of 180° found by Isbekow.

SYSTEM $MgBr_2AlBr_3$

Anhydrous $MgBr_2$ was prepared from a c.p. sample of the hexahydrate by the method proposed by Liebig.[3] $MgBr_2\ 6H_2O$ forms a stable equimolecular compound with NH_4Br, which upon gentle heating first loses all of the water of hydration, leaving the compound $MgBr_2$, NH_4Br. By raising the temperature this compound is decomposed; and after strong heating only $MgBr_3$ is left. The product so obtained gave only a very slight basic reaction, indicating practically no decomposition to oxide.

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[1] Isbekow and Plotnikow, loc. cit.
[2] See Roozeboom, loc. cit.
[3] Liebig, Pogg. *19* 137, (1830).

No previous work on this system could be found in the literature. Data are given below.

(a) Solid phase—$AlBr_3$.

%$MgBr_2$.	0.00	0.6	1.4
T.	97.1	96.8	96.5

(b) Solid phase—$2AlBr_3,MgBr_2$-(?).

%$MgBr_2$.	0.6	1.4	3.8	8.1	12.9	18.4	21.6	23.5
T.	134.9	160.7	190.2	199.6	210.5	221.6	227.9	231.5

Tubes with more than 24% $MgBr_2$ could not be brought into solution by prolonged heating at 360°. The solid phase separated in fine crystals, probably the neutral salt by comparison with the action of the monovalent metal systems already given. It will be noted that the curve rises rapidly with only small %'s of $MgBr_2$, a fact noted in many of the systems which follow.

One new compound was found; probably $2AlBr_3$, $MgBr_2$, since this is the one found most frequently in the systems with the divalent bromides which follow. This is the first case encountered where transition to the next phase occurs at such a composition as to make the true nature of the compound uncertain. To remove this uncertainty it would be necessary to analyze the solid phase as has been done in previous work.[1,2]

The transition of the compound occurs at 233°.

SYSTEM $CaBr_2$-$AlBr_3$

The salt used was prepared from a U.S.P. sample by recrystallizing once from distilled water and carefully decomposing the hydrate (hexa). The salt after drying in an oven at 120° for several hours was placed in a Pyrex tube and fused to insure the complete removal of water. The product so obtained showed only a slight basic reaction and was used without further purification. Extra precautions were again[3] observed in the preserving of the salt and the preparation of tubes for this system, due to the very deliquescent nature of anhydrous $CaBr_2$.

No previous work on this system is reported.

The data are given below and in Fig. 2.

(a) Solid phase—$AlBr_3$.

%$CaBr_2$.	0.00
T.	97.1

(b) Solid phase—$xAlBr_3,yCaBr_2$.

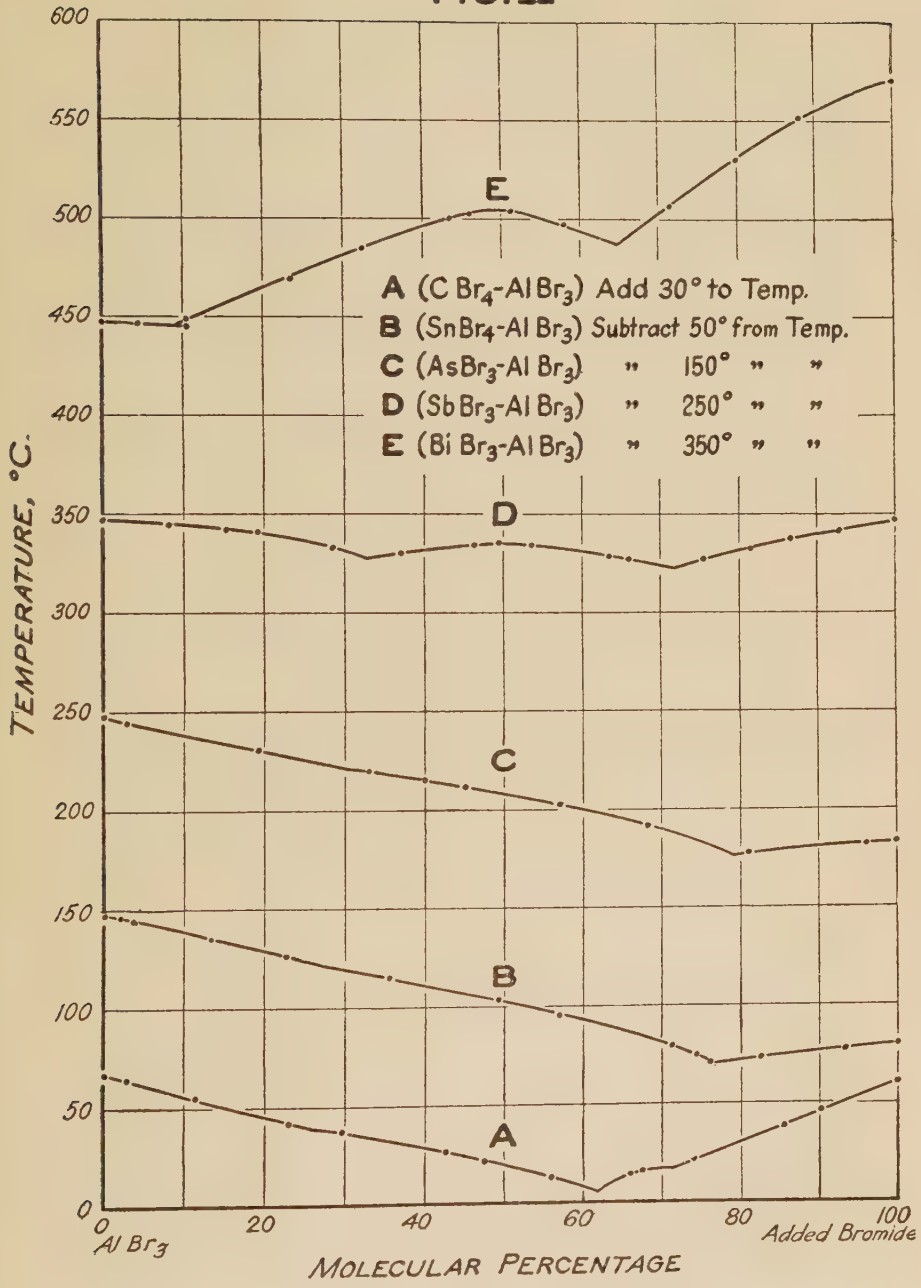
%$CaBr_2$	0.74
T.	204.2

[1] Davidson, Columbia University Dissertation, (1920). Also Adler, loc. cit.

[2] Due to the very hygroscopic nature of the two salts involved, it was thought best not to attempt analysis on the solid phase, but to be satisfied with the information given by the freezing point curve. This was the policy adopted throughout this work.

[3] See note under lithium system above.

FIG. IV


600
550
500
450
400
350
300
250
200
150
100
50
0
TEMPERATURE, °C.
E
D
C
B
A
A (C Br4-Al Br3) Add 30° to Temp.
B (Sn Br4-Al Br3) Subtract 50° from Temp.
C (As Br3-Al Br3) " 150° " "
D (Sb Br3-Al Br3) " 250° " "
E (Bi Br3-Al Br3) " 350° " "
0
Al Br3
20
40
60
80
100
Added Bromide
MOLECULAR PERCENTAGE

(c) Two liquid layers; solid phase disappears at 208°.8.
No temperatures of mixing could be determined for this system as even the low percentages coalesced at temperatures above 300°.

(d) Solid phase—$xAlBr_3,yCaBr_2$.

%$CaBr_2$.	15.4
T.	195.3

(e) Solid phase—$2AlBr_3,CaBr_2$.

%$CaBr_2$.	16.05	18.9	21.4	24.3	27.3	30.95	33.8
T.	213.1	229.5	242.6	260.1	276.8	298.4	304.9

(f) Solid phase—$CaBr_2$.

%$CaBr_2$.	33.8
T.	398.0

It was impossible to bring more than 34% of $CaBr_2$ into solution even at 450°. The curve is rising rapidly even at this composition, as was the case with the previous systems. The solid phase is undoubtedly $CaBr_2$.

There is an unstable compound in the two layer region as evidenced by the two eutectic points, one on either side of the two layer region. The compound $2AlBr_3$, $CaBr_2$ is just stable at its maximum and has a melting point of 306°.

SYSTEM $BaBr_2$-$AlBr_3$

The salt used was a c.p. sample recrystallized once from distilled water and dried at 120°.

Isbekow and Plotnikow[1] report that this salt is insoluble in aluminium bromide. The present work shows that this is not the case. These writers probably mistook for pure $BaBr_2$ the solid phase —$2AlBr_3,BaBr_2$—which separates even in the lower percentages. Since the curve rises steeply to the two layer region where the solid phase disappears at 269°.4, this error in interpretation can be readily explained.

The data for this system are given below.

(a) Solid phase—$AlBr_3$.

%$BaBr_2$.	0.00
T.	97.1

(b) Two liquid layers; solid phase disappears at 269°.4.
As with $CaBr_2$, no temperatures of coalescence could be determined.

(c) Solid phase—$2AlBr_3,BaBr_2$.

%$BaBr_2$.	.88	12.0	15.2	18.3	21.2	24.2	28.03
T.	269.4	269.4	269.4	276.7	292.0	310.0	335.0

The lower limit of the two layer region could not be determined by means of closed tubes, so was not attempted. One new compound, very likely $2AlBr_3$, $BaBr_2$, similar to the one with $CaBr_2$, has been found. On account of the high temperature, no percentages higher than twenty-eight were made up.

[1] Isbekow and Plotnikow, loc. cit.

SYSTEM $ZnBr_2$-$AlBr_3$

The salt used was prepared from a c.p. sample by one recrystallization from water. The product after drying at 120° was transferred to a bent Pyrex tube and distilled. The anhydrous salt was quickly placed in a glass stoppered bottle and kept in an oven during use.

Isbekow reports that $ZnBr_2$ gives a completely homogeneous solution with aluminium bromide. A great tendency towards supercooling was found in this system; and hence, although 66% could be readily brought into solution, a glass was formed upon cooling which would not crystallize even after months of standing. Thls same phenomenon made the taking of freezing points in this system especially difficult even with the lower percentages.

Data for this system are given immediately below.

(a) Solid phase—$AlBr_3$.

%$ZnBr_3$.	0.00	2.6	5.6	11.3	14.5
T.	97.1	95.5	94.4	87.6	83.5

(b) Solid phase—$2AlBr_3$, $ZnBr_2$.

%$ZnBr_2$.	11.3	12.1	14.5	20.6	26.7	30.0	35.1
T.	95.1	96.1	99.3	104.1	108.8	110.4	110.6

One new compound—$2AlBr_3$, $ZnBr_2$—with a melting point of 111°.5 has been found. On account of the formation of the glasses previously noted, the work was not extended beyond 35%.

SYSTEM $CdBr_2$-$AlBr_3$

The salt used was a c.p. sample recrystallized once from distilled water and carefully dried at 120°.

Isbekow reports that this system gives no two layers, but gives no further data.

Data are given below and in Fig. 3, B.

(a) Solid phase—$AlBr_3$.

%$CdBr_2$.	0.00	0.7
T.	97.1	95.6

(b) Solid phase—$2AlBr_3$,$CdBr_2$.

%$CdBr_2$.	1.1	1.8	4.5	5.2	9.0	11.6	13.04	19.3
T.	140.7	168.1	189.6	190.0	192.9	195.4	197.0	204.2
%$CdBr_2$.	26.0	28.9	33.1	35.3				
T.	217.4	221.2	224.0	223.1				

(c) Solid phase—$CdBr_2$.

%$CdBr_2$.	35.3
T.	234.9

One new compound, $2AlBr_3$, $CdBr_2$, with melting point 224° was found.

This system is especially interesting from the standpoint of the phase rule on account of the marked tendency towards the formation of two liquid layers in the same percentage region where two layers were noted in the systems above. In this system, however, the two

layers exist only in the metastable region,[1],[2] and merely introduces a pushing up of this portion of the curve leading to extreme flatness.

SYSTEM HgBr-$AlBr_3$

Mercurous bromide was prepared by a method exactly similar to the one used to prepare AgBr. This salt was also preserved in a dark place and tubes made up and worked with only in subdued light.

Isbekow reports that this salt is soluble in aluminium bromide to the extent of 3-4% at 220°. This has been confirmed and the system extended beyond 70%.

Data are given below and in Fig. 3, D.

(a) Solid phase—$AlBr_3$.

%HgBr.	0.00	0.6
T.	97.1	96.6

(b) Solid phase—(?), probably $AlBr_3$, HgBr.

%HgBr.	1.2	1.7
T.	161.5	225.4

(c) Two liquid layers; solid phase disappearing at 238°.1.

%HgBr.	3.3	No other points could be determined on account of the
T.	275.5	high temperature and consequent danger of explosion.

(d) Solid phase—$AlBr_3$, HgBr.

%HgBr.	33.9	35.0	40.5	44.4	48.6	53.2	54.7	59.6
T.	242.1	243.9	250.1	255.1	259.7	256.6	252.9	241.4

(e) Solid phase—HgBr.

%HgBr.	62.7	66.1
T.	243.7	281.3

One new compound, $AlBr_3$, HgBr, similar to the one obtained with silver, though less stable, melting at 261°, has been found.

The curve is rising so rapidly at 66% that further work was not attempted. There seems little probability that further compounds exist since the behavior of the higher percentages is strictly analogous to that of silver and lithium.

SYSTEM $HgBr_2$-$AlBr_3$

Mercuric bromide was prepared by the direct action of bromine on mercury which was kept under water to control the action. The salt was recrystallized twice from distilled water and carefully dried. The product was found to melt sharply at 241°.5.

Isbekow reports homogeneous solutions for this system which have been confirmed; also one new compound—$2AlBr_3$, $HgBr_2$, which exists in two crystalline modifications—has been found.

Data for this system are given below and in Fig. 3, A.

(a) Solid phase—$AlBr_3$.

%$HgBr_2$.	0.00	1.44
T.	97.1	95.8

[1] See Miller, loc. cit.

[2] Hildebrand, J.A.C.S., *38* 1452 (1916) discusses the factors which affect immiscibility.

(b) Solid phase—$2AlBr_3$, $HgBr_2$.

%$HgBr_2$.	3.8	4.6	7.1	9.8	10.1	13.7	17.9	20.1
T. (Stable)	94.3	....	95.9	....	96.7	98.7	100.1	....
T. (Unstable)	....	93.5	94.7	95.8	....	....	99.1	100.1
%$HgBr_2$.	25.8	28.7	31.4	32.2	32.85	37.7	40.3	
T. (Stable)	102.8	103.6	104.1	....	103.9	103.1	101.9	
T. (Unstable)	101.9	102.5	....	102.6	....	....	100.7	

(c) Solid phase—$HgBr_2$.

%$HgBr_2$.	44.2	45.2	49.4	59.6	62.8	75.7	83.1	88.0
T.	118.8	123.2	145.5	175.0	183.6	206.8	217.1	224.4
%$HgBr_2$.	94.0	98.1	100.0					
T.	232.9	239.1	241.5					

The compound—$2AlBr_3$, $HgBr_2$—existing in two crystalline forms is stable well beyond its maximum, but is not a very stable compound, as evidenced by the flatness of the curve around 33%. The melting points of the two modifications are: stable, 103°.9; unstable, 102°.8. In the tubes of higher composition there was considerable darkening which made the taking of melting points more difficult, but the reproducibility was well within the limits established above.[1] In the diagram (Fig. 3, A.) only the points for the stable form of the compound are plotted.

SYSTEM TlBr-$AlBr_3$

Thallous bromide was prepared by precipitating a solution of c.p. HBr with pure thallous sulfate. After thorough washing by decantation, the precipitate was transferred to a filter paper and again washed to remove all sulfate. The salt was carefully dried at 120° and then heated to 200° to insure the decomposition of any compounds between TlBr and HBr. The salt so prepared is light yellow in color, resembling freshly precipitated AgBr. The salt, although not ultra pure, was deemed of sufficient purity for this investigation.

No previous work on this system could be found. The data are given below and in Fig. 1, A.

(a) Solid phase—$AlBr_3$.

%TlBr.	0.00
T.	97.1

(b) Two liquid layers; solid phase disappears at 103°.9.

%TlBr.	0.6	21.4	22.4
T. of Coales.	260°	260°	118.4

(c) Solid phase—x$AlBr_3$, yTlBr.

%TlBr.	24.4
T.	99.9

(d) Solid phase—$2AlBr_3$, TlBr.

%TlBr.	24.4	26.03	26.9	28.4	30.7	32.7
T.	104.4	105.9	106.7	108.1	110.6	111.8

[1] See "Precision of Measurements."

(e) Solid phase—$AlBr_3$, TlBr.

%TlBr.	35.4	37.6	40.0	40.7	42.4	46.3	48.2	51.0
T.	126.8	142.1	157.7	160.4	171.8	192.9	203.4	207.9
%TlBr.	52.1	53.3						
T.	200.8	193.1						

(f) Solid phase—TlBr.

%TlBr.	55.0	55.2
T.	213.8	215.9

The curve is rising rapidly at 55% with the deposition of TlBr.

The resemblance of this system to those of the alkali metals and silver is striking, a point to be discussed more fully after the presentation of results.

Three new compounds: $xAlBr_3,yTlBr$; $2AlBr_3,TlBr$; and $AlBr_3,TlBr$, have been isolated. The first of undetermined composition breaks up into two liquid layers; the second is stable at its maximum, but undergoes transition to the equimolecular compound just beyond this composition. The equimolecular compound is very stable, having a melting point of 210°.

The lower limit of the two-layer region could not be established by the method here employed.

SYSTEM CBr_4-$AlBr_3$

The carbon tetrabromide used[1] in this system was recrystallized once from absolute alcohol and dried in a vacuum desiccator. The product melted sharply at 90°.1, which agrees sufficiently well with the values recorded in the literature[2] to permit its use in this investigation.

This work confirms[3] the existence of two modifications of carbon tetrabromide, with a transition point of 48°.4.[4] Isbekow reports complete miscibility for this system.

No other work on this system could be found. Data are given below and in Fig. 4, A.

(a) Solid phase—$a AlBr_3$.

%CBr.	0.00	1.02	2.7	11.5	23.03
T.	97.1	96.6	94.5	85.7	72.5

(b) Solid phase—$b AlBr_3$.

%CBr_4.	29.5	42.5	47.6	49.5	55.9
T.	68.5	56.7	52.3	50.2	44.0

(c) Solid phase—$b CBr_4$.

%CBr_4.	66.1	67.6
T.	44.7	46.1

(d) Solid phase—$a CBr_4$.

%CBr_4.	73.7	85.5	90.3	100.0
T.	51.7	68.8	77.6	90.1

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[1] The author wishes to express his thanks to Prof. M. T. Bogert for the loan of the sample.

[2] Abegg, Hand. Anorg. Chem. *3* (2) 113. Bolas and Graves, J.C.S., *23* 161 (1870).

[3] Schwarz, Roozeboom, Heterogene Gleichgewicht, *1* 127; Rothmund, Zeit. Phys. Chem., *24* 714 (1897).

[4] The value recorded above is slightly higher than previous ones and could not be checked because of the small quantity of CBr_4 available.

No compounds were isolated, which was to be expected from the non-polar nature of the two salts. The existence of the two forms of aluminium bromide has been confirmed in this system.

SYSTEM $SnBr_4$-$AlBr_3$

Stannic bromide was prepared by the direct action of bromine on powdered tin. The salt was distilled twice from excess tin and preserved in a tightly stoppered flask. The salt crystallizes to a beautiful white solid, melting sharply at 31°.[1]

Isbekow reports complete miscibility for this system, which has been confirmed in this work.

Data are given below and in Fig. 4, B.

(a) Solid phase—*a*$AlBr_3$.

%$SnBr_4$.	0.00	1.9	2.5	13.4	22.7	
T.	97.1	96.0	94.3	85.4	76.4	

(b) Solid phase—*b*$AlBr_3$.

%$SnBr_4$.	35.4	49.2	56.7	71.2	74.4	76.0
T.	65.7	53.7	45.8	29.7	25.5	22.3

(c) Solid phase—$SnBr_4$.

%$SnBr_4$.	82.5	93.3	100.0
T.	23.4	27.6	31.0

The two forms of aluminium bromide noted above are shown to be present in this system. The failure to form compounds is, as would be expected, from the nature of the two components.

SYSTEM $SnBr_2$-$AlBr_3$

The stannous bromide used was prepared by the action of c.p. hydrobromic acid on 30-mesh tin, after the reduction of stannic bromide by excess tin had failed. After the tin was completely dissolved, the solution, which was a bright yellow color, was evaporated to small volume and allowed to crystallize. The crystals, which were a hydrate of a complex compound, $xHBr$, $ySnBr_2$, were freed from mother liquor on a porous plate,[2] transferred to a wide Pyrex tube, sealed at one end, and gently heated to drive off water and HBr. The temperature was carried well above 300° to insure the complete removal of HBr. The salt, which was pale yellow, was transferred to a glass stoppered bottle and kept in an oven at 120° during use.

The product obtained by the above method contained a small quantity of oxide formed by the decomposition of the complex

[1] Various values between 25°.5 and 33° are recorded in the literature. Thus, Bertholet, Thermochimie, *2* 156 (1897); Carnelley and O'Shea, Chem. News, *36* 264 (1877); Rayman and Preis, Lieb. Ann., *223* 323 (1884).

[2] Attempts were made to crystallize from acetone and alcohol, but resulted in the destruction of both salt and solvent.

hydrate. Several samples from two different preparations melted sharply at 232°. The best previous value which could be found was 215°.5.[1]

No previous work on this system could be found recorded. Data are given bolew and in Fig. 2, C.

(a) Solid phase—$AlBr_3$.

%$SnBr_2$.	0.00	0.35	0.81	1.07
T	97.1	96.9	96.8	96.3

(b) Solid phase—(?), probably $2AlBr_3$, $SnBr_2$.

%$SnBr_2$.	0.8	1.07	1.45
T.	121.6	137.1	152.8

(c) Two liquid layers; solid phase disappears at 161°.1.

%$SnBr_2$.	2.1	3.4	4.7	10.4	10.7	13.34
T. of Coales.	169.1	187.3	198.0	202.4	201.4	185.4

(d) Solid phase—$2AlBr_3$, $SnBr_2$.

%$SnBr_2$.	16.4	16.6	18.5	24.7	28.3	30.7	34.95
T.	162.2	162.7	164.3	178.5	190.2	197.8	202.0

%$SnBr_2$.	41.5	43.7
T.	181.8	175.4

(e) Solid phase—$AlBr_3$, $SnBr_2$.

%$SnBr_2$.	44.8	48.3	52.4	55.2	59.6	62.8
T.	175.0	179.8	179.1	172.9	164.4	158.3

(f) Solid phase—$SnBr_2$.

%$SnBr_2$.	71.2	78.1	82.9	90.8	96.25	100.0
T.	175.1	195.9	206.4	220.9	228.2	232.0

The critical temperature of mixing for the two-layer region is 204°.5.

Two new compounds, $2AlBr_3$,$SnBr_2$ and $AlBr_3$,$SnBr_2$, have been isolated with melting points 205° and 183° respectively. The compound $2AlBr_3$,$SnBr_2$ is the most stable of the two, as evidenced by the sharpness of its maximum in comparison to that of the equimolecular one.

There is no evidence of an unstable compound in the two-layer region, this system resembling the one with silver.

SYSTEM $PbBr_2$-$AlBr_3$

Lead bromide was prepared by a method similar to the one used for HgBr above. The salt was recrystallized once from distilled water and carefully dried at 120°.

No previous work on this system could be found in the literature. Data are given below and in Fig. 2, B.

(a) Solid phase—$AlBr_3$.

%$PbBr_2$.	0.00
T.	97.1

(b) Solid phase (?), probably $2AlBr_3$, $PbBr_2$.

%$PbBr_2$.	0.63
T.	191.9

(c) Two liquid layers; solid phase disappears at 210°.4.

[1] Abegg, Hand. Anorg. Chem., *3* (2) 571.

No temperatures of coalescence could be determined, even those for low percentages lying above the boiling point of $AlBr_3$.

(d) Solid phase—$2AlBr_3$, $PbBr_2$.

%$PbBr_2$.	16.95	20.1	23.7	27.0	30.5	32.5	37.0	39.
T.	211.9	220.4	235.5	253.5	267.7	272.5	266.9	257.
%$PbBr_2$.	43.6	45.5						
T.	241.6	234.9						

(e) Solid phase—$PbBr_2$.

%$PbBr_2$.	52.3	57.7
T.	268.4	296.8

The curve is rising rapidly at 58% with the deposition of $PbBr_2$ as solid phase. There is no evidence of an unstable compound in the two-layer region; this system resembling that of barium above.

One new compound—$2AlBr_3$,$PbBr_2$—has been isolated, which is stable at its melting point, 274°.

SYSTEM PBr_3,$AlBr_3$

The phosphorous tribromide used was an E. & A. sample, twice redistilled. The middle fraction, boiling constantly at 175°, was collected and preserved in sealed tubes, which were opened only long enough to fill one bulb at a time.

Due to the very hygroscopic nature of this compound, the curve could not be carried beyond 50%. Beyond this composition fine crystals, probably $POBr_3$, were deposited, which invalidated the work on higher points. In the region investigated, no compounds were isolated. No previous work on this system could be found. Data are given below.

(a) Solid phase—*a*$AlBr_3$.

%$PbBr_3$.	0.00	7.35	14.4	22.4
T.	97.1	91.3	84.1	76.6

(b) Solid phase—*b*$AlBr_3$.

%PBr_3.	31.5	44.0	48.2	49.1
T.	67.3	53.6	47.0	45.4

The two modifications of aluminium bromide are again apparent in this system.

SYSTEM $AsBr_3$-$AlBr_3$

The arsenic tribromide used in this work was prepared from a "pure" E. & A. sample by two distillations. The middle fraction from the second distillation was taken and preserved in a sealed tube. The salt melted sharply at 32°.8, and was used in the fused condition throughout.

Isbekow reports complete miscibility for these two components. Data for the complete system are given below and in Fig. 4, C.

(a) Solid phase—*a*$AlBr_3$.

%$AsBr_3$.	0.00	5.3	19.3
T.	97.1	94.5	81.1

(b) Solid phase—*b*$AlBr_3$.

%$AsBr_3$.	32.8	40.1	44.8	46.4	56.9	68.05
T.	69.5	65.7	61.9	60.9	52.8	41.7

(c) Solid phase—$AsBr_3$.

%$AsBr_3$.	80.9	96.1	100.0
T.	28.2	32.2	32.8

No compound was isolated in this system, a result to be expected from the nature of the two components. The two modifications of $AlBr_3$ are again shown here.

SYSTEM $SbBr_3$-$AlBr_3$

Antimony tribromide was prepared by a method analogous to the one used in the preparation of aluminium bromide cited above. The product was distilled twice and used without further purification. Samples melted sharply at 96°.6.[1]

Isbekow reports complete miscibility for these two salts. This has been confirmed in this work, as well as finding one new compound, $AlBr_3$, $SbBr_3$, M.P., 85°.2.

Data are given below and in Fig. 4, D.

(a) Solid phase—$AlBr_3$.

%$SbBr_3$.	0.00	8.2	15.2	19.2	28.6
T.	97.1	94.7	92.3	90.3	82.9

(b) Solid phase—$AlBr_3$, $SbBr_3$.

%$SbBr_3$.	37.1	46.5	49.3	53.5	63.5	66.4
T.	80.5	84.2	85.1	84.3	78.8	76.9

(c) Solid phase—$SbBr_3$.

%$SbBr_3$.	72.5	75.7	81.6	86.7	92.8	100.0
T.	72.9	76.3	81.9	86.5	91.3	96.6

That a compound should be found in this system is not surprising after consideration of the conductivity results given by Isbekow and Plotnikow[2] for this system. They find much greater conductivity for antimony tribromide in aluminium bromide than for arsenic tribromide in the same solvent. The values for antimony tribromide rise to a maximum in the vicinity of fifty molecular per cent, as would be expected to be the case[3] if a compound were present, as has been found in this work.

SYSTEM $BiBr_3$-$AlBr_3$

Bismuth tribromide was prepared by the direct action of bromine on metallic bismuth. Due to the slowness of the reaction an apparatus to allow bromine to be continually in contact with the metal was employed.[4] The product, which is bright yellow in color, was dried from the last traces of bromine, placed in a Pyrex tube bent at an angle of 45°, and slowly distilled into the open half of the tube.

[1] Various values are given in the literature. Thus: 90°-94°, Abegg, Hand. Anorg. Chem., 3 (3) 590; 90°, Cooke, J. B., (1877), p. 284; 94°.0, Serullas, Ann. Chim. Phys., *38* 322 (1828).

[2] Isbekow and Plotnikow, loc. cit., p. 335.

[3] See Gross, Columbia University Dissertation (1919) for a discussion of the effect of compound formation on ionization and hence conductivity.

[4] An apparatus with reflux condenser attached was used.

After cooling, the product was recovered by gently tapping the tube. The salt so obtained melted sharply at 220°.4.[1]

Isbekow finds that $BiBr_3$ is completely miscible in all proportions with aluminium bromide. Data for the complete system are given below and in Fig. 4, E.

(a) Solid phase—$AlBr_3$.

%$BiBr_3$.	0.00	4.4	10.6
T.	97.1	96.8	95.5

(b) Solid phase—$AlBr_3$, $BiBr_3$.

%$BiBr_3$.	10.6	23.6	32.5	43.5	46.0	51.1	57.7
T.	98.5	119.2	135.5	150.2	152.0	153.1	147.8
%$BiBr_3$.	65.6						
T.	137.3						

(c) Solid phase—$BiBr_3$.

%$BiBr_3$.	71.5	79.7	88.0	100.0
T.	156.9	180.1	202.7	220.4

One new compound, $AlBr_3$,$BiBr_3$, has been isolated with a melting point of 153°.

The compound with bismuth is much more stable than the corresponding one with antimony, showing that there is an increase in stability of compounds with increasing metallicity of the added component. This point will be taken up under the discussion of results.

SYSTEM $CrBr_3$-$AlBr_3$

Chromic bromide was obtained in black, shining crystals by the direct action of bromine on heated chromium metal. Only a limited quantity could be made by this method; but due to the almost complete insolubility of this salt in aluminium bromide, this was sufficient to determine the limit of solubility.

Less than 0.5% of chromic bromide could be brought into solution at 200°. The result agrees with the results obtained by Miller[2] for the corresponding chloride system.

SYSTEM $MnBr_2$-$AlBr_3$

Anhydrous manganous bromide was obtained from a "pure" E. & A. sample by recrystallizing once from distilled water and carefully decomposing the hydrate. The salt was then fused, broken up, and preserved in a glass stoppered bottle in an oven at 120° during use.

Isbekow reports no two layers for this system. In this work the curve was carried to 30%, at which composition the curve was rising steeply with the deposition of $MnBr_2$.

Data are given below and in Fig. 3, C.

(a) Solid phase—$AlBr_3$.

%$MnBr_2$.	0.00	0.68
T.	97.1	96.3

[1] The best previous value recorded is 215°.

[2] Miller, loc. cit.

(b) Solid phase—$2AlBr_3$, $MnBr_2$.								
%$MnBr_2$.	0.68	1.98	4.6	5.65	9.4	13.8	17.5	20.6
T.	127.1	171.6	199.1	199.8	204.6	210.8	217.6	223.8
%$MnBr_2$.	24.0	25.8	28.0	29.6				
T.	232.9	237.7	241.7	242.6				

Tubes with 28% or more $MnBr_2$ separated fine crystals which could not be brought into solution below 300°. This behavior is similar to that noted in the magnesium and cadmium systems above. The flat portion of the curve from 3-9% recalls the case of cadmium especially. This system, as will be noted, shows the tendency towards the formation of two layers never realized in the stable region.

One new compound, probably $2AlBr_3$,$MnBr_2$, by analogy to cadmium, has been found. This compound undergoes transition near 28% to the neutral salt.

SYSTEM $NiBr_2$-$AlBr_3$

Anhydrous nickel bromide was made by treating pure nickel lumps with c.p. HBr. The solution so obtained was filtered, evaporated to small volume, and allowed to crystallize. The crystals of the hydrate were carefully decomposed at 120°, and the partially dry salt heated to 250° to insure the decomposition of any compounds between HBr and $NiBr_2$. The salt was a finely divided, deep-brown powder, resembling Fe_2O_3.

Isbekow reports the complete insolubility of $NiBr_2$ in aluminium bromide. In this work it was found possible to bring 0.54% into solution at 300°, but 0.78% could not be made to dissolve after several hours' heating at 360°.

SYSTEM $FeBr_2$-$AlBr_3$

Ferrous bromide was prepared from a "pure" sample by heating in a Pyrex tube, slowly, at first, to decompose the hydrates, and finally by raising the temperature to 500°. The product, although of rather doubtful purity, was deemed of sufficiently good quality to test the solubility for this system. Tubes with ferrous bromide were deep red in color, which made the taking of exact melting points exceedingly uncertain. As far as could be determined from the relative melting points on a few tubes, the curve resembled that given by magnesium, and more especially cadmium. The curve is rising rapidly at first with the deposition of fine crystals followed by a flat portion indicating a tendency toward the formation of two layers. This type of curve might be expected from the position of ferrous iron in the "electrode potential" series, since it is only slightly below cadmium.

The limit of solubility lies near 20%, for 20.8% could not be brought into solution after heating at 300° for an hour.

No previous work on this system could be found recorded in the literature.

DISCUSSION OF RESULTS

(a) Compounds Isolated.

The double salts isolated in this investigation are given below in Table I. Only one compound—$AlBr_3$,KBr—has been previously reported. The elements in the table are arranged in the order as found in the periodic system.

TABLE I

Li—7$AlBr_3$,LiBr; 2$AlBr_3$,LiBr; $AlBr_3$,LiBr.
Na—x$AlBr_3$,y$NaBr$; 7$AlBr_3$,2$NaBr$; 2$AlBr_3$,$NaBr$; $AlBr_3$,$NaBr$.
K—x$AlBr_3$,yKBr; 2$AlBr_3$,KBr; $AlBr_3$,KBr.
NH_4—x$AlBr_3$,yNH_4Br; 3$AlBr_3$,NH_4Br; 2$AlBr_3$,NH_4Br; $AlBr_3$,NH_4Br.
Ag—2$AlBr_3$,$AgBr$; $AlBr_3$,$AgBr$.
Ca—x$AlBr_3$,y$CaBr_2$; 2$AlBr_3$,$CaBr_2$.
Ba—2$AlBr_3$,$BaBr_2$.
Mg—2$AlBr_3$,$MgBr_2$.
Zn—2$AlBr_3$,$ZnBr_2$.
Cd—2$AlBr_3$,$CdBr_2$.
Hg′—$AlBr_3$,$HgBr$.
Hg″—2$AlBr_3$,$HgBr_2$.
Tl′—x$AlBr_3$,y$TlBr$; 2$AlBr_3$,$TlBr$; $AlBr_3$,$TlBr$.
C—None.
Sn″ ″—None.
Sn″—2$AlBr_3$,$SnBr_2$; $AlBr_3$,$SnBr_2$.
Pb—2$AlBr_3$,$PbBr_2$.
P″ ′—None.
As″ ′—None.
Sb—$AlBr_3$,$SbBr_3$.
Bi—$AlBr_3$,$BiBr_3$.
Cr″ ′—None.
Mn″—2$AlBr_3$,$MnBr_2$.
Ni—None.
Fe″—2$AlBr_3$,$FeBr_2$, (?).

In agreement with the main point of the theory (e.g., 'diversity' factor), the number and complexity of the compounds isolated decreases to a minimum with elements near aluminium in the electrode potential series and increases again below this metal. Thus we find the alkali metal bromides giving the greatest number and the most complex compounds with aluminium bromide. With magnesium,

compound formation has fallen off considerably, for we find only one compound and that with a very narrow range of stability. With tin and lead well below aluminium we find compound formation has increased in extent and continues to do so until we reach a maximum again in the silver system. It becomes apparent from a consideration of the above table that in fused salt mixtures just as in the systems previously investigated that the diversity of the positive radicals is the main factor influencing the formation of addition compounds; although compound formation in salt mixtures is much more influenced by subsidiary factors (e.g., atomic volume, unsaturation, valence) than in any systems previously studied. Thus we find that solubility in the present systems reaches a minimum with nickel and chromic bromides, salts of metals well below aluminium in the electrode potential series; while zinc and magnesium bromides are much more soluble in aluminium bromide than would be the case if the diversity factor were the only one exerting an effect. The small atomic volume of these latter elements suggests that this factor is exerting a counterbalancing effect. This point will be discussed under a separate heading below.

Throughout this investigation, the type of compound isolated is strikingly dependent upon the valence of the metal in the added bromide. Thus we find with the univalent metals (e.g., silver, potassium, thallium) that the equimolecular compound is by far the most stable; although, as was to be expected, other compounds are present. With the divalent metals (e.g., calcium, cadmium, magnesium), the predominant type of compound is $2AlBr_3,MBr_2$; while with the trivalent elements such as antimony and bismuth, we find a return to the equimolecular type. In the case of the quadrivalent elements (e.g., tin and carbon), we find no apparent tendency towards compound formation.[1]

Here again, as in previous work,[2] the temperature of fusion of the added component has a marked effect on solubility. The higher lies the fusion point of the added salt, the less is the solubility. Thus nickel bromide is far less soluble in aluminium bromide than is ferrous bromide; although, from their respective positions in the electrode potential series, we should expect relatively the same solubility. Further illustrations of this behavior are obtained by a comparison of the solubilities in aluminium bromide of barium with calcium bromide, lead with stannous bromide, and mercurous with mercuric bromide.

Unsaturation, which is also a subsidiary factor in compound formation distinct from the factor of valence mentioned above, has a marked influence in the case of thallous bromide. Thus this compound would be expected to have a relatively low solubility in alumi-

[1] This does not necessarily mean that unstable complexes do not exist in the solution. See Kendall, Booge, and Andrews, J.A.C.S., *39* 2303 (1917).

[2] Davidson, loc. cit.

nium bromide from the position of the metal in the electrode potential series. However, we find this salt has a solubility of the same order as that of the alkali metals, which must be accounted for by the unsaturated character of the thallium atom in thallous compounds. This same factor likewise leads to the formation of a larger number of compounds in the case of thallium above and also in the case of stannous bromide. (See Fig. 2, C.) This point will be found more fully discussed by Miller[1] in a comparison of solubilities in chloride and bromide systems.

One further point needs to be mentioned before passing to the discussion of specific factors; namely, the effect of increasing atomic weight on compound formation. As has been pointed out by Abegg and Bodlander,[2] the tendency towards combination increases with increasing atomic weight. This is strikingly shown by a comparison of the systems of the fifth group of the periodic system (i.e., the phosphorous family) with aluminium bromide. Thus, disregarding phosphorous whose action could not be completely determined,[3] and comparing the last three members (i.e., arsenic, antimony, and bismuth), we find that compound formation regularly increases. There is no indication of a compound with arsenic, only a very unstable equimolecular one with antimony, but a very stable equimolecular one with bismuth. This same effect is apparent in the systems of lead and stannous tin. (See Fig. 2, Band C.) Thus we find the $2AlBr_3$, MBr_2 compound in these systems is much the stabler in the lead system as well as having the widest range of existence.

(b) Immiscibility and Internal Pressure.

Low solubility accompanied by the formation of two liquid layers has been observed for similar portions of the curve in several systems above. This phenomenon, although frequently observed in systems of organic liquids with water,[4] has never been so clearly noted for fused salt mixtures. In order to make clear why such a phenomenon should be observed in certain systems and not in others, it is necessary to inquire into the rules which may be said to govern immiscibility in general.

Hildebrand and his co-workers[5] have shown that in any complete study of solubility certain factors of a purely physical nature must be taken into account along with the chemical factors (e.g., compound formation) ordinarily accepted as governing solubility rela-

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[1] Miller, loc. cit.

[2] Abegg and Bodlander, Zeit. Anorg. Chem., *20* 453 (1899); *39* 330 (1904).

[3] It seems highly improbable that any compounds exist in the region which was not investigated when we consider the slightly polar nature of the two compounds.

[4] The most familiar case of this kind is found in the system phenol-water. For other cases see Roozeboom, Heterogene Gleichgewicht, *2* (2) 168.

[5] Hildebrand, J.A.C.S., *38* 1470 (1916); *30* 2297 (1917); *41* 1067 (1919); *42* 2180, 2213 (1920).

tions. The most important of these purely physical factors are internal pressure and 'polar'[1] nature, which will be discussed in light of the present investigation.

By internal pressure is understood the force which with the external pressure opposes the thermal pressure arising from the kinetic energy of the molecules. Expressed in terms of Van der Waal's equation, it is the a/v^2 term. As has been pointed out by Hildebrand, this quantity, although a fundamental one, is not experimentally determinable, but can be obtained by indirect means only. Various methods for calculating this quantity have been proposed by several investigators,[2] leading to rather diverse values. From a consideration of these correlated values, Hildebrand was able to lay down several general rules regarding solubility which may be summarized as follows: (1) The solubility of a non-polar substance in a non-polar liquid of equal internal pressure is that calculated on the basis of Raoult's law. (2) When the internal pressures are unequal, the solubility is less, depending upon the difference of internal pressure. (3) When one substance is polar and the other non-polar, the solubility is less than that indicated by Raoult's law. (4) When both substances are polar (leading frequently to the formation of isolable compounds), the solubility is usually greater than that indicated by Raoult's law.

In general, fused salts are highly polar, leading often to high association factors and frequently to excellent conductivity in the fused condition. Their internal pressures are high as a rule, resulting in low solubility in organic solvents, but leading to high solubility in water and other fused salts. From time to time cases have arisen where pure salts in the fused state have been found to be poor conductors and have low dielectric constants, a manifestation of slightly polar nature and low internal pressure. Thus aluminium bromide[3] in the fused state is practically a non-conductor, as are also stannic bromide and mercuric chloride. As a rule salts of those elements near the center of the periodic system are poorer conductors in the fused state than those of more diverse elements.[4]

In Table 2 below are given the values for internal pressures of the bromides used in this investigation in so far as data are available for their calculation. The values, though merely relative (being in error as much as a thousand atmospheres in some cases), are nevertheless accurate enough to make comparisons valid.

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[1] For a discussion of 'polar' nature, see Bray and Branch, J.A.C.S., *35* 1440 (1913), and Lewis, ibid., *35* 1448 (1913).

[2] Walden, Zeit. Phys. Chem., *66* 385 (1909); Traube, ibid., *68* 291 (1909); Mathews, J. Phys. Chem., *17* 603 (1913); Lewis, Phil. Mag., *28* (6) 104 (1914).

[3] Isbekow and Plotnikow, loc. cit.

[4] Of all salts the alkali halides, exactly those whose radicals are most diverse, are the best conductors in the fused state.

TABLE 2

Substance	Internal pressure	Method
$SnBr_4$	1770 atmos.	Hildebrand[1]
PBr_3	2230 "	"
CBr_4	2300 "	"
$AlBr_3$	2550 "	"
$AsBr_3$	2820 "	"
$SbBr_3$	3240 "	"
$HgBr_2$	4400 "	Van Laar[2]
$BiBr_3$	4860 "	Hildebrand
$SnBr_2$	8990 "	"
$ZnBr_2$	9550 "	"
HgBr	10000 "	Van Laar
$CdBr_2$	10700 "	Hildebrand
KBr	21700 "	"
AgBr	25000 "	"
NaBr	28400 "	"
LiBr	35600 "	"
[3]$CaBr_2$	No data	

From this table it becomes at once apparent that there is as wide a range of internal pressure for fused salts as has been found for organic substances,[4] With salts of nearly the same internal pressure (e.g., stannic tin, carbon, arsenic) aluminium bromide gives completely miscible solutions, as is to be expected. When the internal pressure of the added salt, however, has reached a value of nearly 10,000 atmospheres, we find the type of curve given by cadmium[5] (See Fig. 3, B) where there is a marked tendency toward the formation of two liquid layers never realized[6] in the stable region.

In some cases in point of fact (e.g., mercurous and stannous), even when the internal pressure of the added salt is 10,000 atmospheres, we find two distinct layers. With salts whose internal pressures are greater than ten thousand atmospheres, we obtain a two layer region which may or may not contain an unstable compound[7]

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[1] Wherever possible the equation given by Hildebrand, J.A.C.S., *41* 1067 (1919 was used. The equation is: $p = 20.65\ (5200 + 30t_b)/V_{20}$, where "$p_I$" is the internal pressure, t_b the boiling point of the compound, and V_{20} the molecular volume at 20°.

[2] Van Laar, J. de Chim. Physik., *14* 3 (1916) gives the method for finding the value of a for some compounds which makes it possible to determine the internal pressure by the a/v^2 relation.

[3] Judging from the high temperature of fusion of this and the following compounds: TlBr, $PbBr_2$, $BaBr_2$, and $FeBr_2$, their internal pressures undoubtedly lie above 12,000 atmospheres.

[4] See table of relative internal pressures given by Hildebrand, loc. cit.

[5] The similar behavior of manganese and magnesium makes it seem likely that the internal pressures of these bromides are nearly the same as that of cadmium.

[6] See Miller, loc. cit. for an interesting case of this kind.

[7] See notes under the silver and sodium systems.

The rule of Hildebrand that the greater the difference in internal pressure the greater is the immiscibility is completely justified in the case of the fused salt mixtures studied above. Certain minor discrepancies are to be noted in some few systems, a result to be expected from the present uncertain position of fused salts in Hildebrand's theory. The action of zinc bromide in not giving two layers, although its internal pressure is similar to that of stannous bromide, must be referred to the atomic volume factor discussed immediately below.

Before passing to the next topic, it might be well to call attention to the fact that in all cases where two layers are noted this region occurs with the higher percentages of aluminium bromide. This is best explained by pointing out that it is only in this region that we are truly comparing the internal pressure of aluminium bromide with that of the added bromide; since with higher percentages we are forced to compare the internal pressure of a compound such as $xAlBr_3,yMBr$ with that of another compound or else to that of the pure added component. The effect of adding a substance of low internal pressure to one of high internal pressure, especially if a compound is formed, is to make the internal pressure of the compound higher than that of the lowest pressure constituent.

(c) Solubility and Atomic Volume.

Another subsidiary factor which must be dealt with in light of this investigation is the effect of the atomic volumes of the metallic constituents upon solubility data as well as ionization in so far as the latter can be predicted from this work. This factor has been the subject of numerous investigations[1] in the past few years. Of these brief mention, in passing, needs to be made of the work of Holmes. This writer has attempted to show that there is a close relation existing between the ratio of the diameters of the molecules and immiscibility. He presents numerous cases to show the validity of his claim, but since he has completely neglected the motion of the molecules due to their kinetic energy, his work is of little value for comparisons here.

W. L. Bragg[2] has recently advanced his "Law of Atomic Diameters" in which he postulates spherical atoms with fixed diameters for all elements as determined by crystal structure measurements. He advances the idea that the diameter of a molecule of a compound is the sum of the diameters of its respective atoms. Pease[3] takes exception to this, pointing out the necessity for considering the configuration of the respective atoms as well. The value of the atomic diameter factor apart from the atomic volume factor in solubility relations is taken up by Miller[4] in his discussion of solubility in

[1] Holmes, J.C.S., *103* 2147 (1913), also J.C.S., *113* 263 (1918); Harkins and Hall, J.A.C.S., *38* 194 (1916); Richards, J.A.C.S. *43* 1584 (1921).
[2] W. L. Bragg, Phil. Mag., (6) *40* 169 (1920).
[3] Pease, J.A.C.S., *44* 769 (1922).
[4] Miller, loc. cit.

chloride and bromide systems. All that needs to be mentioned here in this connection is that where the difference in the atomic diameters of the positive radicals is large, the tendency towards immiscibility is far greater. Thus the alkali metals (e.g., sodium, potassium) whose atomic diameters are great in comparison with that of aluminium, form two layer regions as pointed out above; while zinc with an atomic diameter of the same magnitude as aluminium does not give two layers in the system studied above.

The main point to be discussed here is the relation between atomic volume and compound formation, and its bearing upon ionization in so far as the latter can be judged from the present work. The anomalous behavior of lithium bromide in not giving two liquid layers with aluminium bromide must be referred to this factor. Certain rules only briefly presented before will be first taken up in greater detail.

If we compare elements of the same type (i.e., with the same number of electrons in the outer shell), then we should expect those with smaller atomic volumes, owing to the greater attractive forces at the surface, to give addition compounds with neutral molecules more readily than those with larger atomic volumes, where the attractive forces at the surface are relatively weak. This expectation is in accordance with the actual facts. Thus lithium has the smallest atomic volume of any of the alkali metals; and lithium ion is more highly hydrated in aqueous solution than the sodium or potassium ion. In the same way magnesium salts are more highly hydrated in solution than the corresponding compounds of calcium, barium, or strontium. Those metals which exhibit exceptionally small atomic volumes (e.g., aluminium, cobalt and platinum) are exactly those which give salts conspicuous in the formation of molecular complexes (e.g., the alums, the cobaltamines and the platinocyanides).

In the case of lithium bromide, which does not form two liquid layers with aluminium bromide as would be expected from the great difference in the internal pressures of these two salts, we must look to the atomic volume factor for an explanation of this behavior. We are dealing here with two metals both with small atomic volumes, and hence the tendency towards the formation of molecular complexes is unusually high; in fact, so great that the electrical forces at the surface of the molecules are sufficient to overcome the difference in internal pressure tending to cause immiscibility. Although, as has been pointed out previously, the complexities arising in the case of fused salts make an explanation of their behavior uncertain, yet it seems evident in the case just cited that we can ascribe the action to one single factor, i.e., atomic volume.

The abnormally high solubility of zinc and magnesium bromides

in aluminium bromide must be ascribed to this same cause; since, if the diversity factor were the only criterion of their action, we should expect minimum solubility of these salts in aluminium bromide.

As a final illustration in this connection, the exceptional behavior of fluorine in the series of the halogens may be considered. Although fluorine is the *most* electronegative member of this series, hydrogen fluoride exhibits less ionic instability (in other words is less "polar") than the remaining hydrogen halides. This abnormality may logically be ascribed to the small atomic volume of fluorine.[1] On the other hand, this small atomic volume also induces the formation of molecular complexes (e.g., hydrofluosilicic acid, potassium hydrogen fluoride) to a much greater extent than is the case with the other hydrogen halides.

The next consideration is the effect of atomic volume on the ionic instability of the complexes. Whatever view we hold as to the constitution of the atom, the fact remains certain that the constraint on an electron at the surface of a charged atom increases with decreasing atomic volume.[2] Hence with positive atoms of large volume (e.g., the alkali metals) separation of electric charges should take place much more readily than with atoms of small atomic volume such as carbon. As a matter of fact we find that the compounds of the alkali metals followed by those of the alkaline earths show the most pronounced tendency towards ionization of all simple compounds, while carbon gives the least "polar."

We have here an important factor which must be considered in any discussion of ionization. Where the atomic volume is large, there is a *maximum* tendency towards ionization, but a *minimum* tendency towards the formation of molecular complexes. On the other hand, where the ionic volume is small, the original tendency towards ionization is less, but a greater tendency is evidenced towards the formation of molecular complexes; the "ionic instability" of which is regularly more pronounced than that of the simple salt, as has already been shown.[3]

Ultimately, of course, the "diversity" factor (i.e., the difference in positive and negative nature of the constituent radicals) dealt with fully in previous work, must be referred to this basic question of ionic volume, since the "electrode potential" of any element against a standard concentration of its ions will be fundamentally dependent upon the "structure" of the atom; this structure determining the mag-

[1] See Langmuir, J.A.C.S., *41* 907 (1919).

[2] Close up to a charged sphere, the electric force is related to the radius of the sphere and will be greater at the surface of a small sphere than at that of a large one.

[3] Kendall and Gross, J.A.C.S., *43* 1416 (1921).

nitude of the forces existent between the nuclear charge and the exterior electrons, thus making the electrode potential a function of the atomic volume. Our knowledge of the inner fabric of the atom is far too fragmentary at present to allow us to establish any definite quantitative connection between the "diversity" and atomic volume factors. However, it is interesting and important to recognize the fact that, in general, the elements with very large atomic volumes are grouped at the positive and negative extremities of the electromotive series, while those with very small atomic volumes are collected around the center.

SUMMARY

In the present investigation freezing point curves for twenty-five different bromides in aluminium bromide as a solvent have been determined. From an examination of the curve so obtained, it is evident that as in previous work of this kind the "diversity" factor (i.e., the difference in character of the positive radicals as measured by their position in the "electrode potential" series) is again the *governing* factor in the formation of addition compounds between fused salt pairs. Thus the most extensive compound formation was found with the alkali metals, falling off as the positive radical approached aluminium, and increasing to a second maximum with silver.

In this work on fused salts it has been shown that it is necessary to take into account more fully than in previous work the effect of certain subsidiary factors such as internal pressure, atomic volume, unsaturation, valence and temperature of fusion of the pure components which often exercise a counterbalancing on the ordinary course of compound formation and solubility. The effect of internal pressure and atomic volume have been fully discussed.

During the course of the investigation thirty-two new compounds have been isolated and a new modification of aluminium bromide has been discovered.

VITA

Eugene D. Crittenden was born at Saline, Michigan, on May 1, 1898, where he attended the grammar and high schools. From 1915-1919 he attended Michigan State Normal College, receiving his A.B. degree in December, 1919. During the last three years there he was assistant in Chemistry.

In 1918 he was sent to the Officers' Training Camp at Fort Sheridan, Ill., receiving the rank of 2nd Lt. Inf. in September of that year.

In 1920 he entered the graduate school of Columbia, holding a lecture assistantship in Chemistry. In June, 1920, he received his Master's degree and is at present an instructor in General Chemistry at Columbia.

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